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INVENTOR(S)			
Given Name (first and middle (if any))	Family Name or Surname	Residence (City and either State or Foreign Country)	
FLORA TAK TAK GARY LLEWELLYN BONGANI	NG REMPER NKOSI	WATERLOO, ONTARIO, CANADA WATERLOO, ONTARIO, CANADA VANDERBIJLPARK, SOUTH AFRICA	
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto			
TITLE OF THE INVENTION (240 characters max) COMPOSITE CATALYST FOR THE SELECTIVE OLIGOMERIZATION OF LOWER ALKENES AND THE PRODUCTION OF HIGH OCTANE PRODUCTS			
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Respectfully submitted,

SIGNATURE

TYPED or PRINTED NAME David E. Schwartz

TELEPHONE

(703) 415-2555

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P19SMALL/REV05

# COMPOSITE CATALYST FOR THE SELECTIVE OLIGOMERIZATION OF LOWER ALKENES AND THE PRODUCTION OF HIGH OCTANE PRODUCTS

## FIELD OF THE INVENTION

5           This invention relates to the oligomerization of lower alkenes by catalytic distillation. More specifically, the invention relates to a catalytic composite as a catalyst and packing media in a catalytic distillation column for the selective oligomerization of lower alkenes. In addition,  
10 the invention also relates to the hydrogenation of alkenes or of the products from the selective oligomerization to produce high octane products.

## BACKGROUND OF THE INVENTION

          Catalytic distillation (CD) combines catalytic  
15 reaction and separation in a single distillation unit. This idea was first implemented early in the 1920s for the production of esters (Backhaus, 1921) and has been applied to a number of chemical processes based on homogeneous catalysts. The advantages of combining reaction and  
20 separation were not fully appreciated until 1980, when Smith patented a new catalytic distillation technology using heterogeneous catalysts (Smith, 1980).

          Conventional chemical processes that utilise a distillation process (non-catalytic) mainly consist of two  
25 separate unit operations. These include a unit hosting chemical reactions and another unit for separating the different components from the resulting reaction mixture. Under such circumstances, it is difficult to recycle the heat produced by the chemical reaction, and cooling is often  
30 needed to control the temperature in the reaction zone, thus

resulting in ineffective energy utilization in the process. In addition, the productivity of a preferred compound is often limited by the conversion and selectivity in a chemical process due to equilibrium limitations. Since heat and mass transfer resistance are common problems in such a reaction unit, poor catalytic performance may occur together with a shorter catalyst lifetime.

In order to avoid the chemical equilibrium limitation and make full use of reaction heat, the simple combination of a chemical reaction unit with the separation unit in a traditional distillation column has provided a successful approach for a number of catalytic reaction processes. This combination was first utilized for homogeneous reaction systems. Because these systems involve both reaction and distillation, the name reactive distillation (RD) was coined for these processes. The traditional RD processes were mainly based on homogeneous reaction systems; thus, RD is also referred to as homogeneous catalytic distillation. Although RD processes often result in both high reaction rates and high selectivity to certain desired products, several disadvantages still prevail. These include separation of catalyst from the reaction products, recovery of catalyst, column fouling and corrosion. In addition, if the product purity with respect to the catalyst composition is strictly necessary, the products have to be intensively treated after reactive distillation to ensure a satisfactory level of catalyst removal, which can increase operating costs.

For gas and/or liquid reactions occurring on the surface of solid catalysts (heterogeneous systems), reaction products can be easily separated from the catalyst system. If a heterogeneous reaction can be managed within a distillation unit, the difficulty of separation encountered

in homogeneous catalytic distillation can be overcome.  
However, another factor that must be addressed is to ensure  
that sufficient catalyst is placed into the column without  
significantly increasing the pressure drop. It was not  
5 until 1980 that Smith (1980) patented a method of suspending  
catalyst pellets inside a distillation column using  
fibreglass containment bags, which are known as Texas  
teabags. Use of these bags permits the use of heterogeneous  
catalysts without giving rise to large increases in pressure  
10 drop. In contrast to homogeneous catalytic distillation,  
heterogeneous catalytic distillation is preferentially  
termed catalytic distillation.

In the CD process, the solid catalyst has to be  
packed in a suitable manner inside the distillation column  
15 so as to maximize contact between vapour and liquid phases,  
but to minimize column flooding. Indeed, various methods  
have been reported for supporting or containing catalysts  
[Crossland et al., US Patent 5,431,890; Hearn, US Patent  
5,266,546; Sheldon, US patent 5,417,938]. It should be  
20 noted that with all these methods, the catalyst is enclosed  
inside a device which can increase the mass transfer  
resistance of the liquid and gas phases in the column.

Since a catalytic distillation process combines  
heterogeneous reaction and separation in a single  
25 distillation column, the following advantages can often be  
obtained over conventional fixed bed reactors:

- i) The capital and production costs are reduced  
because two operations are combined in a single unit.
- ii) The energy consumption can be minimized as the  
30 heat of the reaction is used for the in-situ vaporization of  
the reactants.

iii) The conversion of the reactant can be enhanced through internal recycling.

iv) As the reaction products are continuously removed from the reaction site or the surface of catalyst as they are formed, the normal chemical equilibrium limitation does not apply, thus allowing a higher conversion to be achieved.

v) The selectivity for a desired product can also be improved by continuously removing of the product away from the reaction site or the catalyst surface as the product is formed.

vi) The heat generated by the reaction can be efficiently carried away by the liquid and vapour, thus eliminating or avoiding the formation of hot spots on or in the vicinity of the catalytic site. This movement of the flushing liquid or vapour has a flushing effect in that it removes the higher molecular weight oligomerization products down from the reaction zone, and thereby freeing the catalytic site for another reaction. The possible fouling and poisoning of the catalyst are greatly reduced.

vi) The catalyst lifetime can also be improved because the catalyst bed is surrounded by hot or boiling liquid and vapour that constantly exert a flushing on the catalyst site. Such a flushing effect remove products and by products that can undergo further reaction which can lead to possible fouling and poisoning of the catalyst.

Although there are many advantages for CD technology over the conventional processes mentioned above, catalytic distillation is not suitable for use in all chemical reaction process. In order to achieve the benefits from a CD process, a chemical reaction system should preferably satisfy the following requirements:

i) The reaction should take place in the liquid phase.

ii) The catalyst should be heterogeneous and stable thermally as well as chemically and physically to retain its structural integrity for maintenance of a long lifetime.

iii) The reaction should be exothermic and in situations where the reaction is equilibrium limited, the CD process presented the option to shift that equilibrium more to the right to achieve higher conversion and higher productivity much more efficiently.

One chemical reaction that satisfies these requirements is the oligomerization of lower alkenes (alkene molecules having from 2 to 6 carbon atoms). Alkylation and oligomerization of lower alkenes was first disclosed by Huss and Kennedy (1990) and Smith et al. (1991). The oligomerization of lower alkenes is an important industrial reaction and represents a route to the production of intermediates used for the production of motor fuels, plasticizers, pharmaceuticals, dyes, resins, detergents, lubricants and additives (O'Connor and Kojima, 1990). With respect to butene oligomerization, the less branched dimer products, octenes, are particularly useful in the manufacture of plasticizers. If heavily branched, the mixture can be used as a gasoline blender.

Historically, the exploitation of all of the C<sub>4</sub> fractions obtained as by-product from hydrocarbon fluid catalytic cracking and steam cracking to produce high value products (high octane value product) has been lacking. Butadiene, a component of the by-product is useful for rubber production and is extracted from the by-product, leaving the remaining C<sub>4</sub> fractions as a mixture referred to



as Raffinate I. The isobutene that is contained in Raffinate I was used as a source for production of methyl tert-butyl ether (MTBE). The remaining components of the C<sub>4</sub> fractions after the removal of isobutene consist mainly of linear C<sub>4</sub> hydrocarbon (butenes) was mainly used as a gasoline blender, albeit a poor one. In certain cases, this product was simply disposed of by flaring. In Raffinate II, n-butene is present at an average content from 70% to 80% and in some cases can be in the ninety percentage ranges. Using this resource, smaller oligomers, particularly C<sub>8</sub> and C<sub>12</sub>, are being produced by current catalytic oligomerization processes.

A variety of butene oligomerization processes have been proposed (Keim et al., 1979; Mathys, 1984; Beltrame et al., 1994) based on homogeneous and heterogeneous reactions. These processes are exclusively focused on the catalyst selection and process optimization so that a high oligomerization rate with a high selectivity to desired products, mainly short and less branched oligomers, can be obtained.

The use of catalytic distillation to enhance the oligomerization of alkenes was first disclosed in US Patent No. 5,003,124 to Smith in 1991. This process utilized an acidic ion exchange resin placed inside a fibre glass bag.

Further research has been carried out in the field of alkene oligomerization, but in most cases, the oligomerization catalyst is contained within a second structure such as cloth or mesh bag, and the reactants have to pass through this structure to access the catalyst. Likewise, the products have to pass through the structure to be removed away from the catalyst. In one such example, Podrebarac (1992) studied butene dimerization in a CD column

using a nickel exchanged zeolite catalyst, where the zeolite was placed directly in fibreglass bags. The zeolite catalyst in this case was quickly deactivated by the production of undesirable long chain oligomers, which  
5 oligomers blocked the active sites on the catalyst. The system also displayed poor selectivity to octane due to the mass transfer resistance caused by the fibreglass bags.

Additional work has been carried out to find alternative methods of placing the catalyst directly in the  
10 reactive zone of the distillation column, without resorting to the containment of the catalyst in secondary structures such as cloth or mesh bags.

US Patent 6,291,719 B1 to Gao et al. discloses dual-functional catalyst structures having very specific  
15 shapes. These catalyst structures, which are formed from a resin catalyst, a metal oxide superacid catalyst or a molecular sieve catalyst, are shown to be suitable for etherification reactions, alkylation reactions, hydrogenation reactions and for the decomposition of MTBE.  
20 US 6,291,719 B1 discloses catalyst structures which are limited to two very specific shapes, and the materials used also possess markedly low surface area values.

US Patent No. 5,244,929 to Gottlieb et al. also discloses moulded organic catalyst bodies made of strongly  
25 acid or basic ion exchange resins.

#### SUMMARY OF THE INVENTION

According to one aspect of the present invention, there is provided a Catalytic Composite wherein the Catalytic Composite is derived from a Catalyst Support  
30 Structure and a catalyst as follows:

- a) Catalyst Supports or Catalyst Carriers made from one or more inorganic oxides such as alumina, silica, titania, and zirconia, including structured materials such as molecular sieves and zeolites or a mixture of structured materials  
5 such as molecular sieves and zeolites with selected inorganic oxides or selected combination of inorganic oxides, and
- b) the Catalyst Supports or Catalyst Carriers in a) above is shaped, formed or moulded into a series of robust structures  
10 referred to as Catalyst Support Structures, and
- c) the Catalyst Support Structures in b) above having a column void volume fraction of from 0.30 to 0.95 when randomly packed in a distillation reactor column, a surface area of from 50 m<sup>2</sup>/g to 500 m<sup>2</sup>/g, and a crush strength of 2.4  
15 to 9.9 kg per unit structure; and
- d) the Catalyst Support Structures with composition, features and properties in a) to c) above, unto which 0.1 to 10.0%, preferably 0.05 to 10% and more preferably 0.1 to 8% by weight of active metal ion is deposited onto the  
20 surfaces and in which the active metal ion is primarily in the oxidation state of I or II or both I and II and the deposited metal ion in such oxidation states is referred to as the catalyst; and which said combination of Catalyst Support Structure and catalyst is herein referred to as  
25 Catalyst Composite.
- e) the Catalyst Support Structures with composition, features and properties in a) to c) above, unto which 0.01 to 10%, preferably 0.05 to 10%, and more preferably 0.1 to 8.0% by weight of active metal ion is deposited onto the  
30 surfaces and in which the active metal ion is converted into the zero oxidation state and in such oxidation state is

referred to as the catalyst; and which said combination of Catalyst Support Structure and catalyst is herein referred to as Catalyst Composite.

f) The Catalyst Support Structures of (a) to (c) loaded with  
5 active metal ion described in (d) where the metal ion species is derived from salts of metal sulphate or metal chloride; a mixture of either salts of metal sulphate or metal chloride with ammonium sulphate; mixture of metal sulphate or metal chloride with ammonium chloride. The  
10 resulting composite is also referred herein as the Catalyst Composite.

g) The Catalyst Support Structures of (a) to (c) loaded with active metal ion described in (e) where the metal species is derived from a metal complex or an organometallic  
15 complex where the ligand in such complex is a simple organic molecule or inorganic molecule that does not contain sulphur or phosphorous and is unstable in the temperature range of 100 to 500°C and also decomposable in such temperature range. The resulting composite is also referred herein as the  
20 Catalyst Composite.

The second aspect of the invention relates to the application as a packing media in a reaction apparatus where the reaction apparatus is a catalytic reaction tower or a catalytic distillation apparatus wherein the Packing media  
25 comprising:

a) the Catalytic Composite which is randomly packed in a catalytic distillation apparatus producing, by virtue of the form of the Catalytic Support Structure, a bed in the distillation apparatus with "column" void volume  
30 fraction of from 0.30 to 0.95 or

b) a homogenous mixture comprising of the Catalytic Composite and one or more of the Catalytic Support Structures in an appropriate ratio randomly packed in a catalytic distillation apparatus to produce a bed in the distillation apparatus with "column" void volume fraction ranging from 0.30 to 0.95.

According to a third aspect of the present invention, there is provided a process for the oligomerization of lower alkenes and in particular, the oligomerization of mixtures of C<sub>4</sub> alkenes, components of Raffinate II, to a hydrocarbon product with a very high C<sub>8</sub> selectivity (weight fraction of octenes including methylheptenes, dimethylhexenes and trimethylpentenes out of the total oligomers average over 80%), which process comprises contacting of the lower alkenes with the Catalytic Composite of the Catalytic Distillation Packing in a catalytic distillation apparatus; reaction of the alkenes with the active catalyst deposited on the Catalytic Composite under catalytic reaction process conditions; and the separation of the oligomerization products by fractionation throughout the Catalytic Distillation Packing.

According to a fourth aspect of the present invention, there is provided a process for the hydrogenation of alkenes including octenes including methylheptenes, dimethylhexenes and trimethylpentenes produced by the above oligomerization process which process comprises contacting of the alkenes with the Catalytic Composite in a catalytic reaction apparatus, and the recovery of the hydrogenation product from the apparatus.

In a further aspect, the present invention provides a catalytic composite for use in a catalytic distillation apparatus, the catalytic composite comprising:

- 5 a) a support structure, made of a porous material, having a void fraction ranging from 0.30 to 0.95, a surface area of from 50 m<sup>2</sup>/g to 500 m<sup>2</sup>/g, and a crush strength of from 2.4 to 9.9 kg per unit structure, the support structure having a shape selected from a ring, a hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body,
- 10 b) from 0.01 to 10% by weight of a catalytically active species, based on the weight of the catalyst, which is deposited on the support structure.

15 In a further aspect, the present invention provides a process for the selective oligomerization of a lower alkene to a C<sub>6</sub>-C<sub>18</sub> alkene, which process comprises contacting the lower alkene with a catalytic composite as claimed in any one of claims 1 to 17, under catalytic

20 distillation conditions.

In a further aspect, the present invention provides a process for the hydrogenation of an alkene to an alkane, which process comprises contacting the alkene with a catalytic composite as claimed in claim 18, under

25 catalytic distillation conditions.

In a further aspect, the present invention provides a process for preparing high octane compounds, the process comprising:

a) contacting a C<sub>2</sub> to C<sub>6</sub> alkene with a catalytic composite as claimed in any one of claims 1 to 17, under catalytic distillation conditions, to obtain a C<sub>6</sub> to C<sub>18</sub> alkene, and

b) contacting the C<sub>6</sub> to C<sub>18</sub> alkene with a catalytic composite as claimed in claim 18, under catalytic distillation conditions to obtain a C<sub>6</sub> to C<sub>18</sub> alkane having a high octane number.

Specific embodiments of the present invention will be better understood when consideration is given to the following description including examples and tables of data presented therein.

#### DESCRIPTION OF THE EMBODIMENTS

##### *Base Materials for Catalyst Support or Catalyst Carriers*

The catalyst support or catalyst carrier material is selected from certain base materials. For example, inorganic oxides, of which suitable examples include alumina, zirconia, silica, titania and any chemical and physical combinations thereof, such as silica/alumina. Mixtures of structurally designed materials such as molecular sieves and zeolites with selected inorganic oxides are also suitable combination as Catalyst Supports. Of these, alumina is preferred, and  $\gamma$ -alumina is more preferred. The selected inorganic oxides including structurally designed materials are commercially available as powdered materials which serves as the base material for Catalytic Support Structures. An example of a ceramic compound which is suitable as a support material is the Mobil Crystalline Material 41 (MCM41), which has a high surface area (1200 m<sup>2</sup>/g) and uniform mesopores of from 15 to 150 angstroms.

### *Catalytic Support Structures*

The base materials available in powdered form or mixture of base materials selected is capable of being shaped, moulded or otherwise formed into specific structures (herein referred to as Catalyst Support Structures) without compromising the integrity of the materials, for example, without alteration of crystalline state or significantly altering the elemental composition and physical properties. The Catalytic Support Structure preferably takes a specific shape or form, which shape or form is selected from the various shapes such as rings or cylinders, cross or multi partition rings or cylinders with 2 cell, 3 cell and 4 cell partitions, saddles (such as Intalox or Beryl saddles), solid rings or cylinders, spheres, and honey comb bodies (single or double). Additionally, the powdered materials may be deposited, immobilized or coated on a metallic or polymeric material, which has a shape as described above, in order to form a layer covering the said metallic or polymeric structure.

The size of the Catalytic Support Structure can be varied, and different sizes can be used for columns having different dimensions. For example, the cylindrical Catalytic Support Structures can be as large as 5 cm (2 inches) in diameter and as small as 6 mm (0.24 inch). The preferred ratio of length to diameter for these cylinders is 1:1, but this ratio can vary from 1:3 to 3:1.

In addition to the shape or form, the surface area of the catalytic support is important and is a factor taken into consideration when the catalytic support is selected for the formation of the Catalytic Support Structure. Catalyst support with large surface area is highly desirable as the base material for Catalytic Support Structures since the



latter will also exhibit a correspondingly large surface area. The BET surface area of the Catalytic Support Structure can range from 40 to 600 m<sup>2</sup> /g depending on the process, the feed and the reaction. Preferably, the surface  
5 area should range from 60 to 450 m<sup>2</sup>/g, and most preferably, from 80 to 350 m<sup>2</sup>/g.

The Catalytic Support Structure should be robust or strong. The crush strength of the Catalytic Support Structure provides a relative good idea of its strength and  
10 its ability to withstand attrition when subjected to varying pressures and temperatures. The Catalytic Support Structure preferably has a crush strength of from 2.4kg to 9.9kg per unit (i.e. per single structure) or per unit of the Catalytic Composite. The Catalytic Composite is obtained from the  
15 Catalytic Support Structure after the deposit of metal catalyst on its surface.

The column void volume fraction is a feature that directly relates to the Catalytic Support Structure when such structure is randomly packed in a reaction column (catalytic  
20 distillation column). The shape or form of the Catalytic Support Structure determines the column void volume fraction, which represents the fraction of space in the column not occupied by the solid portion of the Catalytic Support Structure. The shape or form of Catalytic Support  
25 Structure influences the void volume in two ways. Firstly, the space formed or enclosed within a hollow (volume enclosed wholly or partially) of the Catalytic Support Structure. Secondly, the space generated by the non-uniform orientation (relative angles assumed) of the Catalytic  
30 Support Structure and interaction among the individual Catalytic Support Structure when randomly loaded in the reactor column. The non-uniform orientation of the Catalytic Support Structures does not significantly hinder

the overall flow of the liquid or vapour within the column, which is for practical purposes unidirectional, but it does provide a random distribution as gases or liquid flow through the packed structures. Such a flow pattern enhances gas or liquid contact with the Catalytic Support Structures, which permits a better conversion of vapour to liquid within the void spaces in the column and also lowers the mass transfer resistance through the reactive zone of the distillation column.

- 10 A void fraction of 1.0 represents a completely empty column, while void fractions of 0.30 and 0.95 represent 30 and 95 percent of empty space in the column, respectively. The void fraction within the column which holds the Catalytic Composite or a combined mixture of Catalytic Composite plus Catalytic Support Structures can range from 0.30 to 0.95. Preferably, the void fraction is from 0.40 to 0.85, and more preferably the void fraction is from 0.55 to 0.70. For example, a Catalyst Composite in the form of a cylinder having a 6mm length and 6mm outer diameter gives a column void fraction of 0.50.

The void volume, non-uniform orientation and interaction of the structures that produce a haphazard flow pattern, the resultant control of the reaction by dilution of the amount of catalyst in the column, and the simultaneous

- 25 fractionation and separation of the product collectively contribute to the selectivity of the reaction product in the column. These features can therefore be seen or defined as properties of the Catalytic Composite or properties a homogenous mixture of the Catalytic Composite and the Catalyst Support Structures when randomly packed in a column. Alternatively, these features can be termed as the random packing characteristics of the Catalytic Distillation Packing when the Catalytic Composite or a homogeneous

mixture of the Catalytic Composite and the Catalytic Support Structures is used as such.

The surface features of the Catalytic Support Structures affect the amount of catalyst that can be loaded on such  
5 structure. Surfaces that are rendered smooth or non porous or glazed by the shaping process or otherwise, are undesirable for depositing a wide percentage variation of catalyst loadings. Only traces of catalyst (less than .01%) were found on smooth or low porosity structures. This is  
10 most likely due to the fact that the sites that accommodate the catalyst are blocked by the shaping process. A certain level of surface unevenness or roughness aids in the loading of the catalyst while a distribution of pore size is desirable to achieve a wide range of catalyst loadings. BET  
15 adsorption studies of Catalytic Support Structures and Catalyst Composite derived from alumina rings used herein showed both mesopores and micropores. Pore diameter ranges from 70 angstrom to less than 20 angstrom. The adsorption studies indicated that the catalyst are mostly to be found  
20 in the mesopores of the structure.

#### The Catalytic Composite

The Catalytic Composite is comprised principally of two separate components namely; the Catalytic Support Structure, and an active metal or metal ion species (catalyst). These  
25 are combined or synthesised by a procedure to produce a composite material without the loss of features and properties comprising of both components to constitute or form the Catalytic Composite.

Various catalytically active species can be  
30 deposited on the Catalytic Support Structures described above to constitute the Catalytic Composite. Examples of

active species include metal and metal ions from Group VI, VII and VIII. These metal or metal ions are loaded from the metal salts or metal complexes. Of these, nickel ions loaded from nickel salts, which are especially effective for the  
5 oligomerization of lower alkenes, are preferred as the active species for oligomerization. More preferably, are the nickel ions loaded from aqueous solutions of nickel sulphate, or aqueous solutions of nickel chloride and ammonium sulphate are used as the active catalytic species.  
10 As the oligomerization is acid catalysed, acid and acidic salts can be deposited on the support and used as catalyst. In addition, the oligomerization catalysts comprising nickel ions can be further enhanced through exposure to solutions of ammonium sulphate, sulfuric acid, and toluenesulfuric  
15 acid. Such solutions are herein referred to as catalyst enhancer.

The catalytically active species are not necessarily metallic, as certain salts, such as ammonium sulphate, can be used. Further more, use of ammonium sulphate as a  
20 catalytic species is preferred for the dimerization of isobutylene and the subsequent hydrogenation of the produced trimethylpentenes using Pd on the catalytic composite in the same reaction chamber.

Metal loaded from metal complexes of palladium, platinum,  
25 rhodium and nickel are effective for hydrogenation of alkenes including hydrogenation of octenes and methyl substituted pentenes produced by the oligomerization of butenes by the nickel catalyst herein described. Metal salts can also be used a catalytic species in the  
30 hydrogenation process if the metal ions derived from the salts ca be reduced to give metal species that are active.

The amount of catalyst species on the Catalytic Support Structure is dependent on the concentration of metal salt or the metal complex in solution and to a lesser extent on the length of the exposure period of the Catalytic Support

5 Structure to the solution.

A Catalytic Composite for use as an oligomerization catalyst can, for example, contain nickel in an amount of from 0.1 to 8% by weight, relative to the weight of the composite. Preferably, the amount of nickel is from 0.2 to 6.0% by

10 weight, and more preferably, a nickel content of 0.5% to 5% by weight.

A Catalytic Composite for use as a hydrogenation catalyst can, for example, contain palladium in an amount of from 0.1 to 8% by weight, relative to the weight of the composite.

15 Preferably, the amount of palladium is from 0.2 to 6.0% by weight, and more preferably, a palladium content of 0.5% to 5% by weight.

Deposition of the metal ions on the Catalytic Support Structure to act as a catalyst can be effected by methods

20 known in the art. Examples of such methods include wet and dry impregnation methods, vaporization methods, absorption techniques, ion-exchange techniques, sol-gel techniques and vapour deposition techniques. A description of one such technique is given in example 1 a and b.

25 The Catalytic Composite of this invention with such combined features and properties of both components acts as both, a catalyst for a reaction and a medium for fractionation and product separation.

30 Catalytic Distillation Packing

The Catalytic Composite is effective as a material or a media for the application as Catalytic Distillation Packing when used in a catalytic distillation column because of the large surface area of the composite and the void space obtainable when the composite is randomly packed in the column. The catalyst component of the Catalytic Composite carries out the desired chemical reaction or reactions while the surface area and the void volume is effective for fractionation and separation of the reaction products. The composite can therefore act a catalyst as well as a fractionation medium. Depending on the type of reaction, the activity of the catalyst, or the level of separation that is desirable; the Catalytic Composite can be homogeneously mixed with Catalytic Support Structures (N.B Catalytic Support Structures do not contain catalyst and is inert to reaction )and be used in the catalytic distillation column as Catalytic Distillation Packing. The combination of Catalytic Composite with Catalytic Support Structures as Catalytic Distillation Packing material in a catalytic distillation column can result in an increase in the selectivity of the catalytic distillation process. This increase in selectivity is due to: i) an increase in the void space in the distillation column, and ii) better control on the rate of conversion within the distillation column. For example in the present invention the composite catalyst made from Raschig rings 6mm, combined with Intalox saddles (catalytic support structure) in a 1:1 ratio to form a homogeneous mixture and used as the Catalytic Distillation Packing. Such mixture randomly packed in the column produced a fraction void space of 0.55 which is intermediate between that of the rings (0.49) and the saddles 0.62. The presence of such of Catalytic Support Structures as an inert packing material and Catalyst Composite in the reactive zone can also lead to a better control of the rate of conversion

within the distillation column. For exothermic catalytic reactions, there is the possibility that the temperature will increase uncontrollably as the heat produced by the reaction increases the rate of reaction in an exponential manner. This is commonly referred to as "temperature runoff" or "temperature runaway". Temperature runoff is especially detrimental to the selectivity of certain reactions, such as oligomerization reactions, as higher temperatures result in the formation of unwanted products, such as the formation of polymers instead of oligomers such as dimers. Using support structures as inert packing material within the reactive zone can therefore be beneficial, as they can be used to control or lower the overall rate of conversion in the distillation column by finely dispersing the catalytic composite within the reactive zone. The Catalytic Support Structure as an inert packing material, in effect, act as a dilution medium for the Catalytic Composite and at the same time provides the additional necessary surface for fractionation to occur. The ratio of such inert packing material to Catalytic Composite can be varied for different catalytic active species. The ratio of inert packing material to Catalytic Composite can be, for example, range from 10:1 to 1:10.

The Catalytic Support Structure to be used as inert packing material can be selected from any known packing material that is suitable for use in catalytic distillation. This packing material can have various shapes, such as Raschig rings, Pall rings, penta rings, wagon wheels, honeycomb rings, berl saddles, Intalox saddles, Super Intalox saddles, Hy-Pak packing, Tellerette packing, Maspac packing, Cascade mini-rings, and Nutter rings. The size of the random-packing material used is dependent on the size of the diameter of the distillation

column, and it is usually similar in size to the catalytic composite. The inert packing material can be made out of materials similar to those used for the Catalytic Support Structure, such as alumina, zirconia, silica, and titania, 5 but it can also be formed out of less porous materials such as silicon carbide, metals, ceramic, and plastics.

#### *Reactants and Products*

In the description, the expression "lower alkenes" 10 refers to alkene molecules that have 2 to 6 carbon atoms. Of primary interest are those alkenes that have 4 carbon atoms (1-butene, 2-butene, and isobutene).

The products of the selective oligomerization process of the present invention are principally the dimers 15 and trimers of the  $C_2$  to  $C_6$  alkenes. These products include alkenes having from 6 to 18 carbon atoms, although the products of most interest are the dimers of the  $C_4$  alkenes. These have the general formula  $C_8H_{16}$ , and they are widely used in the petroleum industry as gasoline additives. The 20 possible dimers of  $C_4$  include trimethylpentenes, n-octenes, dimethylhexenes and methylheptenes, of which dimethylhexenes and trimethylpentenes are of greater interest. These two latter products can be hydrogenated to give compounds having high octane values. Trimethylpentenes can be hydrogenated 25 to 2,2,4 trimethylpentane, which has an octane number of 100.

#### *Process Setup and Optimization*

The process of the invention is termed "selective", as the catalytic distillation process using the 30 Composite Catalyst or the Composite Catalyst with the



Catalytic Support Structure permits a reaction that is selective in generating and removal of octenes from butenes from the reaction stream. In conventional oligomerization reactions, many products are formed and the resulting

5 mixture of products has to be purified to isolate the desired product. The production of the mixture also limits the overall selectivity of the reaction. With catalytic distillation however, the process variables can be selected so as to encourage the production of predominately a single  
10 product or group of products. The process variables can also be selected to control the reaction and to prevent intermediate products that would have normally continued to react under conventional reaction conditions to continue to react.

15 Many process variables can be changed when carrying out a CD process, and most of the variables can be optimized for specific reactions or products. Such variables include the position of the feeding inlet, the position of the reactive zone, the operating pressure, and  
20 the feed rate.

#### Position of Feed Inlet

The position of the feed inlet is important as it determines where in the reactor CD column the lower alkene feed stock is introduced and where the reaction commences within the CD  
25 column. For the dimerization of 1-butene, it is preferable to have the inlet for the introduction of the 1-butene in the CD located below the catalyst zone or the reactive zone of the column in order to obtain higher selectivity and productivity as compared to when the inlet was located above  
30 the catalyst zone or reactive zone (Table 8). For the oligomerization of isobutylene, however, it is more advantageous to feed above the catalytic zone (Table 9).

The reaction following introduction of the feed stock above or below the catalyst zone produces a different temperature profile along the catalyst zone and this in-turn affects the conversion and selectivity. The situation is same for  
5 isobutylene and shown in example 7.

The position of the reactive zone, and therefore of the catalytic composite, in the column can also be varied to optimize the reaction. For the selective dimerization of butene, it is preferred to keep the reactive zone fairly  
10 high in the column, as the lower sections usually have a high liquid phase temperature. This high temperature can result in a faster reaction, which favors the formation of large oligomers instead of dimers.

#### The Effect of Operating Pressure

15 The operating pressure within the column can also be varied to optimize the CD process. Variation of pressure in the column will change the temperature, and the pressure is therefore chosen such that the temperature in the reaction zone is suitable for the chemical reaction to occur and such  
20 that a liquid phase is maintained in the reaction zone. For the dimerization of butene, the operating pressure can be, for example, from 90 to 115 psi, with higher pressures increasing the butene conversion. However, care must be taken as increasing the pressure beyond a certain level can  
25 compromise octene selectivity.

#### The Effect of Feed Rate

The feed rate of the reactant can also be varied to optimize the reaction. High feed rates lead to higher production rates, but they can also have a negative impact on the  
30 selectivity of a reaction. In the oligomerization of  $C_4$ , the selectivity of the  $C_3$  product decreases as the feed rate

increases because the reaction has a greater tendency to proceed to products of higher molecular weight such as  $C_{12}$ . In the present invention, the feedstock is preferably mixed with an inert solvent before being fed into the reactor.

- 5 The presence of the inert solvent reduces the concentration of the reactant in the column, thus permitting a higher selectivity in the reaction. Suitable solvents that can be used include  $C_4$  to  $C_8$  alkanes, higher alkanes, cycloalkanes and alkyl substituted cycloalkanes. Preferably, isopentane
- 10 is used as the inert solvent. In addition, the inert solvent uniformly dissipates the heat generated by the reaction and it assists in the extraction and removal of any higher oligomers or coke precursors that could deactivate the catalyst. As long as the mass transfer resistance is
- 15 kept fairly low, which can be achieved by using the catalytic composite of the invention, the separation of the product produced by the distillation column provides good selectivity, even under higher feed rates.

#### Multiple Catalysts and Multiple Catalyst or Reactive Zones

- 20 The catalytic distillation column can also be fitted with more than one catalyst or more than one Composite Catalyst, with or without the use of Catalytic Support Structure as inert media if so desired, within the same reactive zone to carry out more than one reaction simultaneously.
- 25 Alternately, the column can be set up to have two reactive zones, in which each zone may contain a different catalyst or a different Catalytic Composite, with or without the Catalytic Support Structure if so desired, and in which each zone will be subjected to different temperatures.
- 30 profile within the column. These reactive zones filled with different catalysts or different Catalytic Composite and operating at different temperatures within a single column can therefore carry out more than one reaction and as a

result the column is being made to carry out more than one process. This can be used, for example, when dimerization and hydrogenation is required e.g. dimerization of butene and hydrogenation of octene. In such case, one of the  
5 reactive zone may consist of Composite Catalyst such as that given in example 1 and the other consisting of a Composite Catalyst with a hydrogenation catalyst species such as platinum or palladium. Also, such multiple catalysts and multiple Catalyst composites in one or more than one  
10 reactive zones can be used for the dimerization of different alkenes such a 1-butene and isobutylene.

Multiple catalytic distillation columns can also be combined to carry out parallel of concurrent reaction processes. This can be used, for example, for the  
15 concurrent dimerization of two or more of 1-butene, 2-butene and isobutene. This process can be difficult to carry out with a single column, as isobutene dimerizes in the presence of catalyst at a temperature much lower than 1-butene. Two columns can thus be used, where the reactive zones in each  
20 column is placed at a different height thus providing reactive zones having different temperatures. The first reactive zone can operate at a lower temperature to dimerize the isobutene, and the remaining 1-butene can then be fed to the second column which has a reactive zone of sufficient  
25 temperature to permit its dimerization. A combination of multiple columns can also be used to carry out different reactions, such as the dimerization and hydrogenation reactions described above.

Single or multiple catalytic distillation columns  
30 can also be used in conjunction with guard beds. The guard beds are useful to separate unwanted reactants from the reactant streams before such streams are introduced to the CD column. For example, such an operation with a guard bed

is useful for a feed stream consisting of butene and butadiene where the dimerization of a butene is required. In such case, butadiene needs to be removed from the feed stream before introduction into the distillation column

5 since it is well known that butadiene can poison the catalyst of example 1 for the dimerization of butene. A guard bed that removes the butadiene by selective adsorption, or that selectively hydrogenates the butadiene to butene can thus be used to pre-treat the feed stream

10 before it is fed into the CD column.

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE 1a: Preparation of Catalyst Composite from Metal Salt

15 A typical Catalytic Composite was prepared by the wet impregnation of nickel sulphate onto a Catalytic Support structure derived from  $\gamma$ -alumina rings having a length and a diameter of 6mm. 13.5g of nickel sulphate hexahydrate was dissolved in 70ml of deionized water. This solution was then

20 transferred to a container (beaker) containing 100g of the Catalytic Support structure ( $\gamma$ -alumina rings). The container was gently tumbled for about 3mins to achieve a uniform contact between the solution and the rings. After an additional 30mins of equilibration on the bench, the rings

25 was allowed to dry in air. This was followed by drying at 110° C for 12hrs. The dried material was then calcined. The rings was placed in a furnace preset at 110° C. The temperature was then ramped at a rate of 5° C/min to a final temperature of 500° C. Calcination was at 500° C for 12hrs

30 after which time the temperature was gradually lowered to room temperature. The Catalytic Composite so obtained was removed and stored in vials for use. The impregnation

procedure was repeated to obtain Catalytic Composites with an average nickel content of 3% by weight.

#### EXAMPLE 1b. Preparation of Catalyst Composite from Metal Complexes

5 The Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is prepared by wet impregnation technique using Palladium (II) acetate. The salt is dissolved in a solution of 50/50 by weight acetone and de-ionized water. Required amount of dried alumina support is then immersed into this solution and the resultant slurry is  
10 then dried using a rotary evaporator with liquid nitrogen trap. The final palladium loading of the catalyst is determined by Oxford Lab-X 1000 (Oxford Instruments Inc.) XRF machine after proper calibration of the instrument with a physical mixture of  $\gamma$ -alumina and Pd(II) acetate. The  
15 impregnated support is then calcined in air at 300 °C for 3 hours. The calcined catalyst is then pre-reduced by hydrogen at 350°C for 3 hours. The prepared catalyst is transferred directly into an air-tight container containing dried HPLC grade n-heptane (treated before in the same way as the  
20 reactant mixture to remove any dissolved oxygen) in a glove bag kept under argon environment. The container is kept in desiccators, which is kept in the glove-bag at argon atmosphere. Any residual air is then removed from the bag by means of a vacuum pump. The bag is then re-filled with  
25 argon. This sample contains 0.7% Pd by weight and it is a hydrogenation catalyst. The data using this catalyst for the hydrogenation of the oligomerization products are given in EXAMPLE 11 and table 14.

#### 30 EXAMPLE 2: Column Operational Set Up and Optimization

The catalytic distillation processes of the examples were carried out on a CD column having a total height of 24 feet, with an inner diameter of 1 inch and a total packing height of 16 feet. The column is principally comprised of a condenser of a total packing height that consists of three segments. An upper non-reactive section, a reaction zone, a lower non-reactive section with a reboiler. The non-reactive sections is filled with Catalyst Support Structure as the inert packing material, such as the  $\frac{1}{4}$ " Intalox saddles, or any other known and suitable Catalytic Support Structures as mentioned before. The use of Intalox saddles in the non reactive zone produced a void volume fraction of 0.62. The reactive zone consists of the Catalyst Composite derived from the alumina rings described in example 1 above, the random packing of which produced a void volume fraction of 0.49. Alternatively, the total packing height may consist of a mixture of the Catalyst Composite and the Catalyst Support Structure. For example the Catalyst Composite derived from the alumina rings of example 1 and Intalox saddles, a 1:1 mixture of which produced a void volume fraction of such 0.55.

The height of the total packing is dependent on the amount of catalyst on the composite and the feed stock which determines the nature of reaction. The catalytic distillation column normally operates at total reflux. The feed stock, for example 1-butene or isobutylene, is mixed with an inert solvent and fed into the column. The inert solvent does not participate in the reaction but is used to dissipate the heat generated by the reaction from the reaction site. The solvent also facilitates the extraction/dissolution and removal of any higher oligomers or coke procurers that could potentially deactivate the catalyst. Depending on the reactants, products and process

conditions for a particular operation, solvent can include butanes, pentane, hexanes, higher alkanes and cycloalkanes and alkyl-substituted cycloalkanes. For example, in the dimerization of butenes, isopentane was found to be an effective solvent. Alternatively, the packing material within the column may be continuous, i.e. not segmented into 3 "zones". The packing material in such a case comprises the catalytic composite of the invention alone throughout the column, it comprises a substantially homogeneous mixture of the catalytic composite with an inert packing material.

The following are additional examples of the effect of various process parameters on the oligomerization of butenes.

EXAMPLE 3. Effect of reboiler duty on the oligomerization of butenes

The effect of reboiler duty on the CD process for the dimerization and oligomerization of 1-butene was investigated by varying reboiler duty from 200 W to 300 W with a 1-butene feed rate of 48.17 g/h, isopentane feed rate of 13.27 g/h, and 79.45 g of a catalyst composite containing 3.0 wt% Ni at a total pressure of 140 psig. The catalyst composite was mixed with an equal volume of  $\frac{1}{4}$  in Intalox saddles. The results obtained are listed in Table 1. It can be seen that when the reboiler duty increases, the reaction zone temperature increases by a few degrees, correspondingly the conversion increases from over 85% to over 95%. Surprisingly although the conversion increases, the selectivity to the octene dimer also increases. When consecutive reactions such as the oligomerization of butenes described in this invention was carried out in a conventional reactor, normally the selectivity to dimers decreases when the conversion increases. However, the



examples showed that when the oligomerization was carried out in a catalytic distillation packing with this catalyst composite with good mass transfer characteristics as described in this invention, the selectivity to the octene dimer unexpectedly also increased with the conversion.

The effect of reboiler duty on the oligomerization of isobutylene was also examined by increasing the reboiler duty from 250 W to 380 W with an isobutylene feed rate of 58.30 g/h, isopentane feed rate of 63.25 g/h, and 75 g catalyst composite containing 1.5 wt% Ni mixed with an equal volume of  $\frac{1}{4}$  in Intalox saddles at a total pressure of 60 psig. The results are listed in Table 2. As the reboiler duty increases, the selectivity to octenes increased from over 65% to about 76 % although the conversion remains essentially the same. This behaviour showed that the feed rate is a little low for 75 g of the catalyst composite since essentially all the isobutylene is converted. This example displayed that an increased reboiler duty leads to an increase in reflux flow rate and a better selectivity for the octene dimers.

For the oligomerization of 1-butene or isobutylene, it is demonstrated that as the reboiler duty increases, the selectivity to octenes increases, which shows that the catalytic composite is effective for both reaction and separation. Since isobutylene is more reactive than 1-butene, a lower system pressure which results in lower temperatures in the distillation column, and a lower Ni loading on the catalytic packing are found to be more suitable for the oligomerization of isobutylene.

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EXAMPLE 4. Effect of operating pressure. Oligomerization of 1-butene

The effect of operating pressure on the oligomerization of 1-butene was investigated by changing the operating pressure from 90 psig to 140 psig, with a 1-butene feed rate of 48.17 g/h, isopentane feed rate of 13.27 g/h, and 142 g of catalyst composite containing 3.0 wt% Ni and mixed with 1.2 times the volume of  $\frac{1}{4}$ " ceramic Intalox saddles. The results obtained for 1-butene oligomerization are listed in Table 3.

On increasing the operating pressure in a catalytic distillation column, the temperature in the reaction zone increased correspondingly. This resulted in an increased conversion of 1-butene from over 90% to about 96%. However, the selectivity to octenes decreased slightly. This could be due to the fact that the chemical reaction is now faster than the mass transfer rate due to the reboiler duty (i.e. the reflux flow rate) used for the experiment was not high enough for this experiments. In our 1-inch distillation column, we could not increase the reboiler duty further due to the problems of flooding the distillation column. Such problems can be avoided in a commercial column.

EXAMPLE 5. Effect of feed rate. Oligomerization of 1-butene

The effect of feed rate on the oligomerization of 1-butene was investigated at first by increasing 1-butene feed rate from 35.31 g/h to 66.37 g/h with 79.45 g catalyst composite containing 3.0 wt% Ni at 140 psig total pressure mixed with an equal volume of  $\frac{1}{4}$  in Intalox saddles (Table 4). The effect was further investigated by increasing 1-butene feed rate from 48.17 g/h to 85.63 g/h with 142 g catalyst composite containing 3.0 wt% Ni and 1.2 times the volume of

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1/2 in Intalox saddles at 140 psig (Table 5). Increasing the feed rate increased the productivity. At the lower feed rate, the productivity is lower, and hence it is advantageous to maximize the productivity per g of catalyst by varying the feed rate. The effect of increasing the isobutylene feed rate from 58.30 g/h to 77.38 g/h with 75 g catalyst composite containing 1.5 wt% Ni and an equal volume of 1/2 in Intalox saddles at 60 psig on the isobutylene oligomerization is shown in Table 6. It can be seen that the productivity also increased as the feed rate was increased indicating that the productivity could be optimized by the changing the feed rate. There is an optimum ratio of catalyst amount and feedrate for maximum productivity in a CD process.

#### EXAMPLE 6. Catalyst stability. Oligomerization 1-butene

The catalyst stability for the oligomerization of 1-butene could be seen in the data shown in Table 7. Over a period of 122 hours, at a reboiler duty of 300 W, 1-butene feed rate of 48.17 g/h, isopentane feed rate of 13.27 g/h, and 79.45 g catalyst composite containing 3.0 wt% Ni and an equal volume of 1/2 in Intalox saddles at 140 psig, the conversion, selectivity and productivity are essentially the same over the 122 h period. These data showed that the catalyst composite is very stable in the CD process for butene oligomerization. After the reaction was terminated, the catalytic composite was removed from the column. It was observed the catalytic composite remains intact indicating the mechanical strength of the composite is suitable for use in the CD column. Surface area measurement of the catalyst composite before and after the oligomerization were 183.7

m<sup>2</sup>/g and 182 m<sup>2</sup>/g respectively, indicating the stability and resistance of the catalyst composite to deactivation.

EXAMPLE 7. Effect of Feed position. Oligomerization of 1-  
5 butene and isobutene.

The position of feed inlet to the distillation column, i.e. whether the feed was above or below the catalyst zone, while all the other process conditions such as pressure, catalytic composite, reboiler duty and feedrate are kept the same,  
10 could also result in a change in productivity and selectivity. This is due mostly to the changes in the temperature profile along the catalyst zone when the feed position is changed and this affects the conversion and selectivity. Examples obtained for 1-butene and isobutylene  
15 are shown in Tables 8 and 9. The results show that variation of feed inlet position will have an effect on productivity and selectivity.

EXAMPLE 8. Comparison of CD and Batch Reactors.  
20 Oligomerization of 1-butene and isobutene.

The advantages of a CD reactor for the dimerization of isobutylene can be seen in Table 10. Under similar reaction conditions such as temperature and reaction time, the conversion and selectivity of the oligomerization reaction  
25 carried out in a CD column is much higher than a batch reactor or a flow reactor. This shows that the catalyst composite containing Ni under CD conditions gives a high conversion and selectivity to the octene dimer compared to a batch or flow reactor system.

EXAMPLE 9. Other Catalytic Active Species for  
Oligomerization of Lower Alkenes

Besides  $\text{NiSO}_4$  as a catalytic component on a porous support  
such as  $\gamma$  alumina, other catalytic material such as  $(\text{NH}_4)\text{Fe}$   
5  $(\text{SO}_4)_2$ ,  $\text{FeSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  are also active for the  
dimerization and oligomerization of isobutylene ( Table 11).

EXAMPLE 10. Effect of Ni salts on the Oligomerization of 1-  
butene

10 Table 12 showed the activity of different Ni compounds on a  
porous support structure, based on  $\gamma$  alumina, for the  
oligomerization of 1-butene. Ni sulphate is more active than  
Ni chloride. Addition of  $\text{NH}_4\text{Cl}$  to  $\text{NiCl}_2$  increased the  
activity of  $\text{NiCl}_2$ . The surface area of the fresh and used  
15 catalyst are not very different indicating that the catalyst  
composites are quite stable. Table 13 shows that for the 1-  
butene oligomerization, the porous  $\gamma$  alumina is much more  
stable than the NaY zeolite or BaNaY zeolite used to support  
the  $\text{NiSO}_4$  or  $\text{NiCl}_2$  as can be seen from the reduction of the  
20 surface area of the used catalyst.

EXAMPLE 11. Hydrogenation of Octenes, Dimethylhexenes and  
Trimethylpentenes

The octenes (dimethylhexene and trimethylpentene) obtained  
25 via oligomerization of butenes were hydrogenated using Pd  
composite catalyst. The reaction was carried out in batch  
mode using a Composite Catalyst that consists of 0.7 wt% Pd.  
Results from this example can be found in Table 16. The  
catalytic composite containing 0.7 wt% Pd is effective for

the 100% hydrogenation of the CD product from the dimerization of isobutylene to 2,2,4 trimethylpentane.

2,4,4-trimethyl-pentene-1 is hydrogenated faster than 2,4,4-trimethyl-pentene-2 and there is isomerization of 2,4,4-trimethyl-pentene-1 to 2,4,4-trimethyl-pentene 2 during the hydrogenation reaction.

#### Preparation of feed stream:

A mixture for the batch reaction containing approximately 95 wt% isopentane and 5% 1-TMP is prepared in a closed tank of 1 L capacity. Nitrogen is bubbled through the liquid mixture for 4 hours via a dip tube, under constant stirring at 100 rpm, to free it from any dissolved oxygen. The tank is then pressurized to 100 psig and kept overnight. It is then depressurised and then pressurized back at 80 psig with nitrogen.

#### Batch Reaction Procedure:

The catalyst is transferred from the catalyst container to the 'catalyst addition device' of the batch reactor inside the glove bag. The reactor is then sealed within the glove bag and purged with argon. The reactor is then removed from the glove-bag and the necessary connections are made. It is then purged with hydrogen to remove any argon present in the reactor. The reactants are transferred from the reactant tank into a sampling bomb. The reactants are then transferred from the sampling bomb to the reactor. The reactor is then set to the desired reaction temperature and pressurized with hydrogen to a pressure that is 50 psig less than the desired reaction pressure. Sufficient time is allowed for the hydrogen to dissolve in the liquid phase. After the desired reaction temperature is reached, the reactor is then pressurised to the desired reaction pressure

and by adjusting the three-way valve in the connecting the catalyst addition device becomes open and the catalyst is dropped into the mixture and the start of the reaction time is noted.

- 5 Table 14 and 15 show that results for hydrogenation of 1-trimethylpentene and 2-trimethylpentene to 2,2,4 trimethylpentane in batch mode between 75 and 125°C. The rate of hydrogenation of 1-trimethyl-pentene was about 10 times faster than the hydrogenation of 2-trimethyl-pentene.
- 10 During hydrogenation of 1- trimethylpentene, some 2- trimethylpentene was also produced through an isomerization reaction. Results for the hydrogenation of alkene products prepared from a CD column using the catalytic composite of the invention are given in table 16. The reactants were a
- 15 mixture of 1-trimethylpentene and 2-trimethylpentene, and the product obtained was mainly 2,2,4 trimethylpentane.

#### The CD Hydrogenation of isomerized product

The reaction parameters along with the percentage conversion for the CD hydrogenation are summarized in table 16.

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- All publications, patents and patent applications cited in this specification are herein incorporated by reference as if each individual publication, patent or patent application were specifically and individually indicated to be
- 25 incorporated by reference. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it is readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

It must be noted that as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Unless defined otherwise all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this invention belongs.



Table 1: Effect of reboiler duty for 1-butene oligomerization

	CD6-V	CD6-IV	CD6-I
<u>Reaction conditions:</u>			
Operating pressure, psig	140	140	140
Reaction temperature, °C	93-111	96-114	97-117
Reboiler duty, W	200	240	300
Amount of catalyst composite, g	79.45	79.45	79.45
Nickel concentration, wt%	3.0	3.0	3.0
Catalyst position, ft	12.5- 14.5	12.5- 14.5	12.5- 14.5
Feed rate of 1-butene, g/h	48.17	48.17	48.17
Feed rate of isopentane, g/h	13.27	13.27	13.27
Feed position	Below	Below	Below
<u>Results:</u>			
Conversion, wt%	85.83	89.80	95.92
Selectivity, wt%	85.25	86.96	87.06
Productivity, g/g-h	0.52	0.54	0.58

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit weight of catalyst composite per hour

Table 2: Effect of reboiler duty for isobutylene oligomerization

	S1CD3	S1CD4	S1CD5	S1CD6
<u>Reaction conditions:</u>				
Reaction pressure, psig	60	60	60	60
Reaction temperature, °C	64-88	62-88	60-87	57-86
Reboiler duty, W	250	300	350	380
Amount of catalyst composite, g	75	75	75	75
Nickel concentration, wt%	1.5	1.5	1.5	1.5
Catalyst position, ft	10.7-12.7	10.7-12.7	10.7-12.7	10.7-12.7
Feed rate of isobutylene, g/h	58.30	58.30	58.30	58.30
Feed rate of isopentane, g/h	63.25	63.25	63.25	63.25
Feed position	Below	Below	Below	Below
<u>Results:</u>				
Conversion, wt%	92.14	93.45	91.64	91.35
Selectivity, wt%	65.14	68.82	73.94	76.20
Productivity, g/g·h	0.72	0.73	0.71	0.71

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit weight of catalyst per hour

Table 3: Effect of operating pressure for 1-butene oligomerization

	CD-7- I	CD-7- III	CD-7- IV
<u>Reaction conditions:</u>			
Operating pressure, psig	90	115	140
Reaction temperature, °C	83-104	94-115	106-122
Reboiler duty, W	300	300	300
Amount of catalyst composite, g	142	142	142
Nickel concentration, wt%	3	3	3
Catalyst position, ft	10.5-14.5	10.5-14.5	10.5-14.5
Feed rate of 1-butene, g/h	48.17	48.17	48.17
Feed rate of isopentane, g/h	13.27	13.27	13.27
Feed position	Below	Below	Below
<u>Results:</u>			
Conversion, wt%	90.91	95.32	95.61
Selectivity, wt%	88.38	87.91	86.66
Productivity, g/g·h	0.31	0.32	0.32

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit weight of catalyst composite per hour

Table 4: Effect of feed rate for 1-butene oligomerization

	CD6- VIII	CD6-I	CD6- VII
<u>Reaction conditions:</u>			
Operating pressure, psig	140	140	140
Reaction temperature, °C	99-118	97-117	91-107
Reboiler duty, W	300	300	300
Amount of catalyst composite, g	79.45	79.45	79.45
Nickel concentration, wt%	3.0	3.0	3.0
Catalyst position, ft	12.5- 14.5	12.5- 14.5	12.5- 14.5
Feed rate of 1-butene, g/h	35.31	48.17	66.37
Feed rate of isopentane, g/h	9.96	13.27	17.69
Feed position	Below	Below	Below
<u>Results:</u>			
Conversion, wt%	96.71	95.92	88.03
Selectivity, wt%	87.27	87.06	87.51
Productivity, g/g.h	0.43	0.58	0.74

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit weight of catalyst composite per hour

Table 5: Effect of feed rate for 1-butene oligomerization

	CD-7- IV	CD7-V	CD7-VI
<u>Reaction conditions:</u>			
Operating pressure, psig	140	140	140
Reaction temperature, °C	106-122	101-122	96-122
Reboiler duty, W	300	300	300
Amount of catalyst composite, g	142	142	142
Nickel concentration, wt%	3	3	3
Location of catalyst, ft	10.5-14.5	10.5-14.5	10.5-14.5
Feed rate of 1-butene, g/h	48.17	66.37	85.63
Feed rate of isopentane, g/h	13.27	17.69	23.23
Feed position	Below	Below	Below
<u>Results:</u>			
Conversion, wt%	95.61	95.40	93.39
Selectivity, wt%	86.66	86.53	87.76
Productivity, g/g.h	0.32	0.45	0.56

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit weight of catalyst composite per hour

Table 6: Effect of feed rate for isobutylene oligomerization

	S1CD4	S1CD7
<u>Reaction conditions:</u>		
Operating pressure, psig	60	60
Reaction temperature, °C	62-88	48-56
Reboiler duty, W	300	300
Amount of catalyst composite, g	75	75
Nickel concentration, wt%	1.5	1.5
Location of catalyst, ft	10.7-12.7	10.7-12.7
Feed rate of isobutylene, g/h	58.30	77.38
Feed rate of isopentane, g/h	63.25	40.25
Feed position	Below	Below
<u>Results:</u>		
Isobutylene conversion, wt%	93.45	90.71
Isooctene selectivity, wt%	68.82	77.94
Productivity, g/g.h	0.73	0.94

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit  
 5 weight of catalyst composite per hour

Table 7: Catalyst stability for 1-butene oligomerization

	CD6- I	CD6- III	CD6-VI	CD6-IX
<u>Reaction conditions:</u>				
Time interval, h	0-41	48-58	84-92	114- 122
Operating pressure, psig	140	140	140	140
Reaction temperature, °C	97-117	96-115	95-114	95-114
Reboiler duty, W	300	300	300	300
Amount of catalyst composite, g	79.45	79.45	79.45	79.45
Nickel concentration, wt%	3.0	3.0	3.0	3.0
Catalyst position, ft	12.5- 14.5	12.5- 14.5	12.5- 14.5	12.5- 14.5
Feed rate of 1- butene, g/h	48.17	48.17	48.17	48.17
Feed rate of isopentane, g/h	13.27	13.27	13.27	13.27
Feed position	Below	Below	Below	Below
<u>Results:</u>				
Conversion, wt%	95.92	96.12	95.63	95.30
Selectivity, wt%	87.06	86.48	86.49	88.29
Productivity, g/g.h	0.58	0.58	0.58	0.58

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit  
weight of catalyst composite per hour

Table 8: Effect of feed position for 1-butene oligomerization

	CD5-I	CD5-II
<u>Reaction conditions:</u>		
Operating pressure, psig	130	130
Reaction temperature, °C	118-	114-
	125	119
Reboiler duty, W	300	300
Amount of catalyst composite, g	84.64	84.64
Nickel concentration, wt%	3.0	3.0
Catalyst position, ft	10.5-	10.5-
	12.5	12.5
Feed rate of 1-butene, g/h	51.60	51.60
Feed rate of isopentane, g/h	14.26	14.26
Feed position	Below	Above
<u>Results:</u>		
Conversion, wt%	94.39	86.89
Selectivity, wt%	70.10	65.46
Productivity, g/g·h	0.58	0.53
C8 productivity, g/g·h	0.41	0.35

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit  
5 weight of catalyst composite per hour



Table 9: Effect of feed position for isobutylene oligomerization

	S1CD4	S1CD9
<u>Reaction conditions:</u>		
Reaction pressure, psig	60	60
Reaction temperature, °C	62-88	55-84
Reboiler duty, W	300	300
Amount of catalyst composite, g	75	75
Nickel concentration, wt%	1.5	1.5
Catalyst position, ft	10.7-12.7	10.7-12.7
Feed rate of isobutylene, g/h	58.30	58.30
Feed rate of isopentane, g/h	63.25	63.25
Feed position	Below	Above
<u>Results:</u>		
Conversion, wt%	93.45	91.47
Selectivity, wt%	68.82	74.97
Productivity, g/g-h	0.73	0.71
C8 productivity, g/g-h	0.50	0.53

Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit  
 S weight of catalyst composite per hour

Table 10: A comparison of the catalyst composite performance among the different types of reactors for 1-butene oligomerization

	Batch reactor	Flow reactor	CD reactor
<u>Reaction conditions:</u>			
Reaction temperature, °C	110	110	101-122
1-butene flow rate (g/h) or its amount (g)	40	13.37	66.37
Catalyst, g	3.0	10	79.45
Catalyst composite type	Ni/ $\gamma$ alumina	Ni/ $\gamma$ alumina	Ni/ $\gamma$ alumina
Ni concentration, wt%	3.0	3.0	3.0
Catalyst size, mm	15	2.0	15
Reaction time or residence time (min)	60	44.88	71.82
<u>Results:</u>			
Conversion, wt%	29.83	71.61	88.03
Selectivity, wt%	78.91	64.81	87.51
Productivity, g/g·h	3.98	1.15	0.74

Residence time: weight of catalyst composite/ mass flow rate of 1-butene

5 Selectivity: weight fraction of octenes out of total oligomers

Productivity: weight of oligomers produced by unit  
weight of catalyst composite per hour

Table 11: Effect of different metal sulfates for isobutylene oligomerization

<u>Reaction conditions:</u>					
Reaction temperature, °C	65	65	65	65	65
Amount of Isobutylene, g	45	45	45	45	45
Amount of catalyst, g	3	3	3	3	3
Catalytic phase	(NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	FeSO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	NiSO <sub>4</sub>	NiSO <sub>4</sub>
Support	γ-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>
Ni concentration, wt%	0	0	0	1.5	3.0
SO <sub>4</sub> <sup>2-</sup> concentration, wt%	10.32	5.18	4.93	2.46	4.91
Reaction time, min	75	60	60	60	60
<u>Results:</u>					
Conversion, wt%	3.67	50.6	33.85	14.20	53.09
Selectivity, wt%	61.63	17.30	46.34	37.97	24.97

Selectivity: weight fraction of octenes out of total oligomers

Table 12: A comparison of catalyst composite performance prepared by different catalytic phases supported on the porous  $\gamma$  alumina in the batch reactor

Catalyst	Support	Nickel loading (wt%)	Reaction conditions	Conversion (wt%)	Selectivity (wt%)	Surface area m <sup>2</sup> /g
NiCl <sub>2</sub>	$\gamma$ Al <sub>2</sub> O <sub>3</sub>	5.53	110°C, 600psi, 2hrs	12.53	93.28	Fresh=183.2 Used=188.5
NiCl <sub>2</sub> +NH <sub>4</sub> Cl	$\gamma$ Al <sub>2</sub> O <sub>3</sub>	5.53	110°C, 600psi, 2hrs	28.85	87.89	Fresh=185.7 Used=190.1
NiSO <sub>4</sub>	$\gamma$ Al <sub>2</sub> O <sub>3</sub>	4.04	110°C, 600psi, 2hrs	36.71	72.15	Fresh=186.5 Used=187.0
NiSO <sub>4</sub>	$\gamma$ Al <sub>2</sub> O <sub>3</sub>	4.04	60°C, 600psi, 2hrs	19.15	77.35	Fresh=186.5 Used=188.3
NiMo	$\gamma$ Al <sub>2</sub> O <sub>3</sub>	>10	110°C, 600psi, 2hrs	19.85	38.11	Fresh=148.1 Used=144.1

5

Selectivity: weight fraction of octenes out of total oligomers

Table 13: A comparison of catalyst performance prepared using different supports in a batch reactor

Catalytic Phase	Support	Nickel loading (wt%)	Reaction conditions	Conversion (wt%)	Selectivity (wt%)	Surface area m <sup>2</sup> /g
NiCl <sub>2</sub>	γAl <sub>2</sub> O <sub>3</sub>	5.53	110°C, 600psi, 2hrs	12.53	93.28	Fresh=183.2 Used=188.5
NiCl <sub>2</sub>	NaY	4.85	110°C, 600psi, 2hrs	52.15	69.51	Fresh=622.9 Used=182.4
NiCl <sub>2</sub>	BaNaY	0.87	110°C, 600psi, 2hrs	39.18	81.58	Fresh=581.5 Used=363.2
NiSO <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	4.04	110°C, 600psi, 2hrs	36.71	72.15	Fresh=186.5 Used=187.0
NiSO <sub>4</sub>	NaY	5.20	110°C, 600psi, 2hrs	41.82	73.26	Fresh=635.8 Used=211.9

Selectivity: weight fraction of octenes out of total oligomers

Tabl 14: A brief summary of results for hydrogenation of 1-TMP in a batch reactor. In all cases the reactant used was same (a mixture of ~ 95 wt% isopentane rest 1-TMP).

Reaction Temperature (°C) (Exp. #)	Pressure (psig)	Weight of the catalyst (g) (Feed Wt, g)	1-TMP Conversion (%) aft r			
			20 minut es	30 minut es	45 minut es	60 minut es
125 (E11)	200	1.15 (91.65)	43.21	57.68	72.05	82.24
100 (E9)	200	1.05 (91.86)	40.24	54.21	66.79	78.56
100 (E10)	200	1.15 (91.48)	40.96	58.71	72.38	82.75
100 (E7)	200	1.308 (91.67)	49.45	64.68	78.40	86.71
75 (E13)	200	1.08 (91.38)	27.29	37.35	51.11	61.44

5

Table 15: Rate of reaction of the corresponding components.

Exp. # 11:

1-TMF rate mole/min/g cat	2-TMF rate mole/min/g cat	3-TMF rate mole/min/g cat
-4.85E-04	4.23E-05	5.07E-04
-4.06E-04	2.07E-05	4.12E-04
-3.40E-04	4.95E-06	3.41E-04
-2.86E-04	-5.70E-06	2.90E-04
-2.23E-04	-1.42E-05	2.40E-04
-1.76E-04	-1.64E-05	2.11E-04
-1.41E-04	-1.52E-05	1.88E-04
-1.15E-04	-1.39E-05	1.69E-04
-9.11E-05	-1.55E-05	1.02E-04
-7.01E-05	-2.24E-05	1.97E-05

Mix. Dens.  
mole/cm<sup>3</sup>  
7.6846E-03  
7.6802E-03  
7.6755E-03  
7.6732E-03  
7.6711E-03  
7.6664E-03  
7.6636E-03  
7.6616E-03  
7.6581E-03  
7.6592E-03

5 Exp. # 9:

1-TMF rate mole/min/g cat	2-TMF rate mole/min/g cat	3-TMF rate mole/min/g cat
-8.30E-04	1.17E-04	7.04E-04
-7.32E-04	6.37E-05	6.05E-04
-5.50E-04	2.54E-05	5.15E-04
-4.14E-04	-1.56E-07	4.33E-04
-2.79E-04	-1.95E-05	3.27E-04
-2.00E-04	-2.26E-05	2.38E-04
-1.52E-04	-1.69E-05	1.69E-04
-1.12E-04	-9.96E-06	1.19E-04
3.04E-05	-2.18E-05	7.48E-05

Mix. Density  
mole/cm<sup>3</sup>  
7.2467E-03  
7.2381E-03  
7.2316E-03  
7.2272E-03  
7.2144E-03  
7.2123E-03  
7.2104E-03  
7.2060E-03  
7.2019E-03

Exp. #10:

1-TMF rate mole/min/g cat	2-TMF rate mole/min/g cat	3-TMF rate mole/min/g cat
-9.48E-04	8.78E-05	8.65E-04
-7.07E-04	4.71E-05	6.87E-04
-5.20E-04	1.79E-05	5.41E-04
-3.79E-04	-1.44E-06	4.22E-04
-2.39E-04	-1.59E-05	2.89E-04
-1.57E-04	-1.78E-05	1.97E-04
-1.11E-04	-1.29E-05	1.33E-04
-7.98E-05	-7.08E-06	8.41E-05
-4.32E-05	-5.96E-06	3.71E-05
1.77E-05	-1.53E-05	-2.12E-05

Mix. Dens.  
mole/cm<sup>3</sup>  
7.2471E-03  
7.2440E-03  
7.2266E-03  
7.2295E-03  
7.2220E-03  
7.2206E-03  
7.2148E-03  
7.2143E-03  
7.2155E-03  
7.2147E-03

10 Exp. # 7:

1-TMF rate mole/min/g cat	2-TMF rate mole/min/g cat	3-TMF rate mole/min/g cat
------------------------------	------------------------------	------------------------------

Mix. Dens.  
mole/cm<sup>3</sup>

-1.03E-03	8.63E-05	8.40E-04	7.2445E-03
-7.47E-04	1.47E-04	6.83E-04	7.2342E-03
-5.27E-04	2.21E-04	5.44E-04	7.2286E-03
-3.63E-04	3.08E-04	4.22E-04	7.2151E-03
-2.05E-04	4.54E-04	2.72E-04	7.2158E-03
-1.19E-04	6.15E-04	1.63E-04	7.2097E-03
-7.91E-05	7.82E-04	9.26E-05	7.2039E-03
-5.83E-05	9.48E-04	6.26E-05	7.2092E-03
-3.19E-05	1.11E-03	7.23E-05	7.2052E-03
2.31E-05	1.25E-03	1.22E-04	7.2002E-03

Exp. # 13:

TIME rate	TIME rate	TIME rate	Mix. Density
mole/min/degC	mole/min/degC	mole/min/degC	mole/cm <sup>3</sup>
-7.22E-04	2.42E-05	7.25E-04	6.7374E-03
-5.55E-04	-2.72E-06	5.74E-04	6.7314E-03
-4.20E-04	-2.05E-05	4.49E-04	6.7275E-03
-3.14E-04	-3.06E-05	3.48E-04	6.7249E-03
-2.00E-04	-3.46E-05	2.34E-04	6.7203E-03
-1.27E-04	-2.96E-05	1.57E-04	6.7196E-03
-8.23E-05	-2.04E-05	1.07E-04	6.7168E-03
-5.47E-05	-1.17E-05	7.14E-05	6.7164E-03
-3.61E-05	-9.75E-06	4.47E-05	6.7156E-03
-1.65E-05	-1.78E-05	1.66E-05	6.7154E-03



Table 16 Batch Reaction Hydrogenation of a Column  
Distillation Product Derived from the  
Oligomerization of Isobutylene

Reaction conditions:

- 5      Temperature: 100 °C  
         Hydrogen pressure = 200 psig  
         Speed of rotation = 300 rpm  
         Amount of CD product taken = 78.58 g.  
         Weight of catalyst taken = 1.05 g  
 10     Wt% of C5 in the reactant = ~ 55%  
         Wt% of 1-TMP in the reactant = ~35%  
         Wt% of 2-TMP in the reactant = ~ 8 wt%

Conversion of 1-TMP, %	Conversion of 2-TMP, %	Time min.
0.0	0.0	0
31.6	15.5	10
55.1	25.1	20
71.6	40.1	30
84.8	61.4	45
92.0	76.8	60
95.4	84.9	75
97.5	91.5	90
98.6	94.7	105
100.0	100.0	120

We claim:

1. A catalytic composite for use in a catalytic distillation apparatus, the catalytic composite comprising:
  - a) a support structure, made of a porous material, having a void fraction ranging from 0.30 to 0.95, a surface area of from 50 m<sup>2</sup>/g to 500 m<sup>2</sup>/g, and a crush strength of from 2.4 to 9.9 kg per unit structure, the support structure having a shape selected from a ring, a hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body, and
  - b) from 0.01 to 10% by weight of a catalytically active species, based on the weight of the catalyst, which is deposited on the support structure.
2. The catalytic composite according to claim 1, wherein the void fraction is from 0.3 to 0.95, the surface area is from 50 m<sup>2</sup>/g to 500 m<sup>2</sup>/g, and the crush strength is from 2.4 to 9.9 kg per unit.
3. The catalytic composite according to claim 1, wherein the porous material is an inorganic oxide.
4. The catalytic composite according to claim 1, wherein the support structure comprises one or more of an inorganic oxide selected from alumina, silica, titania, and zirconia.
5. The catalytic composite according to claim 1, wherein the support structure is made of  $\gamma$ -alumina.
6. The catalytic composite according to claim 1, wherein the support structure is in the shape of a Raschig ring.

7. The Catalytic Composite according to claim 1, wherein the catalytically active species is selected from a group VI metal compound, a group VII metal compound, or a group VIII metal compound.
- 5 8. The Catalytic Composite according to claim 1, wherein the catalytically active species comprises ammonium sulphate in a mixture with one or more of a group VI metal salt, a group VII metal salt, and a group VIII metal salt.
- 10 9. The Catalytic Composite according to claim 1, wherein the catalytically active species comprises ammonium sulfate or nickel chloride in a mixture with one or more of a group VI metal salt, a group VII metal salt, and a group VIII metal salt.
- 15 10. The catalytic composite according to claim 4 or 5, wherein the group VI metal salt, the group VII metal salt and the group VIII metal salt are a metal sulphate or a metal chloride.
- 20 11. The catalytic composite according to any one of claims 3 to 6, wherein the metal or the metal salts are in the ionic state.
- 25 12. The catalytic composite according to claim 1 wherein the catalytically active species comprises group VIII metal and a ligand, wherein the ligand comprises one or more atoms selected from the group consisting of carbon, hydrogen, oxygen and nitrogen.
13. The catalytic composite according to claim 12, wherein the group VIII metal is in the zero oxidation state.

14. The catalytic composite according to claim 1,  
wherein the catalytically active species is ammonium  
sulphate.
- 5 15. The catalytic composite according to claim 1,  
wherein the catalytically active species is an organic  
acid or an inorganic acid.
- 10 16. The catalytic composite according to claim 1,  
wherein the catalytically active species is selected from  
sulfuric acid, phosphoric acid, methanesulfonic acid,  
toluenesulfonic acid, and trifluoroacetic acid.
17. The catalytic composite according to claim 1,  
wherein the catalytically active species is nickel  
sulphate of nickel chloride.
- 15 18. The catalytic composite according to claim 1,  
wherein the catalytically active species is selected from  
palladium, platinum, rhodium and nickel.
19. Use of a catalytic composite as claimed in any one  
of claims 1 to 18 as a packing material in a catalytic  
distillation column.
- 20 20. Use of a catalytic composite as claimed in any one  
of claims 1 to 18 as a catalyst in a catalytic  
distillation column.
- 25 21. A process for the selective oligomerization of a  
lower alkene to a C<sub>6</sub>-C<sub>18</sub> alkene, which process comprises  
contacting the lower alkene with a catalytic composite as  
claimed in any one of claims 1 to 17, under catalytic  
distillation conditions.
22. The process according to claim 21, wherein the  
lower alkene is selected from 1-butene, 2-butene and

isobutene, and the C<sub>6</sub>-C<sub>12</sub> alkene is selected from trimethylpentene, n-octene, dimethylhexene and methylheptene.

23. The process according to claim 21, wherein the  
5 catalytic composite is admixed with inert distillation packing.

24. The process according to claim 23, wherein the ratio of the catalytic composite to inert distillation packing is from 10:1 to 1:10.

10 25. The process according to claim 23 wherein the catalytic composite and inert distillation packing are used in separate zones of the catalytic distillation column.

26. The process according to claim 21, wherein the lower alkene is a C<sub>4</sub> alkene and the C<sub>6</sub> to C<sub>18</sub> alkene is  
15 predominantly a C<sub>8</sub> alkene.

27. The process according to claim 26, wherein the octene is a trimethylpentene.

28. A process for the hydrogenation of an alkene to an alkane, which process comprises contacting the alkene with  
20 a catalytic composite as claimed in claim 18, under catalytic distillation conditions.

29. The process according to claim 28, wherein the alkene is selected from trimethylpentene, n-octene, dimethylhexene and methylheptene.

25 30. The process according to claim 28, wherein the catalytic composite is admixed with inert distillation packing.

31. The process according to claim 30, wherein the ratio of the catalytic composite to inert distillation packing is from 10:1 to 1:10.

5 32. The process according to claim 30 wherein the catalytic composite and inert distillation packing are used in separate zones of the catalytic distillation column.

33. The process according to claim 28, wherein the alkene is trimethylpentene, and the alkane is trimethylpentane.

10 34. A process for preparing high octane compounds, the process comprising:

a) contacting a C<sub>2</sub> to C<sub>6</sub> alkene with a catalytic composite as claimed in any one of claims 1 to 18, under catalytic distillation conditions, to obtain a C<sub>6</sub> to C<sub>18</sub> alkene,

15 b) contacting the C<sub>6</sub> to C<sub>18</sub> alkene with a catalytic composite as claimed in claim 18, under catalytic distillation conditions, to obtain a C<sub>6</sub> to C<sub>18</sub> alkane having a high octane number.

20 35. The process according to claim 34, wherein the process steps a) and b) are carried out in a single catalytic distillation column.

36. The process according to claim 34, wherein the process steps a) and b) are carried out in separate catalytic distillation columns.

25 37. The process according to claim 34, wherein the C<sub>2</sub> to C<sub>6</sub> alkene is a C<sub>4</sub> alkene and the C<sub>6</sub> to C<sub>18</sub> alkene is a C<sub>8</sub> alkene.

38. The process according to claim 37, wherein the  $C_8$  alkene is trimethylpentene.

39. A process for preparing high octane compounds, the process comprising:

- 5 a) contacting isobutylene with a catalytic composite as claimed in any one of claims 1 to 18, under catalytic distillation conditions, to obtain trimethylpentene,
- b) contacting trimethylpentene with a hydrogenation catalyst under batch reaction conditions or under hydrogenation  
10 reaction conditions to obtain trimethylpentane.

40. A process for the production of a  $C_6$ - $C_{18}$  alkene, which process comprises contacting the a mixture of  $C_4$  alkenes with a catalytic composite as claimed in any one of claims 1 to 17, under catalytic distillation conditions.

- 15 41. A process for the selective oligomerization of a lower alkene to a  $C_6$ - $C_{18}$  alkene, which process comprises contacting a mixture of  $C_1$  to  $C_6$  alkenes and  $C_1$  to  $C_6$  alkanes with a catalytic composite as claimed in any one of claims 1 to 17, under catalytic distillation conditions.

- 20 42. A process for the hydrogenation of butadiene, the process comprising contacting butadiene with a catalytic composite as claimed in claim 13 or 18, under catalytic distillation conditions.

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# ABSTRACT

The present invention relates to a) a catalytic composite comprising a support structure and a catalytic species that is deposited on the support structure, b) a process for the  
5 selective oligomerization of lower alkenes, which process comprises contacting the lower alkenes with the catalytic composite in a catalytic distillation apparatus and under catalytic distillation conditions, and c) a process for  
10 producing high octane products, which process comprises hydrogenating one or more alkenes through contact with the catalytic composite in a catalytic distillation apparatus and under catalytic distillation conditions.